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Concepción Collar

Significance of viscosity profile of pasted and gelled formulated wheat doughs on bread staling

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Abstract Pasting profile during cooking and cooling of straight/soured started bread doughs formulated with non fat-sodium carboxymethylcellulose (CMC), hydroxypropylmethylcellulose (HPMC), fungal α -amylase and fat-monoglycerides (MGL), diacetyl tartaric acid ester of mono-diglycerides and sodium stearoyl lactylate (SSL) additives was recorded in the Brabender (BVA) viscoamylograph and Newport rapid viscoanalyser (RVA). Rheological results were correlated with bread staling kinetics during storage. Bread dough viscosity characteristics, derived from the RVA pasting profile during cooking and cooling, highly correlate with bread staling kinetic parameters. This is particularly so in the cases of peak viscosity, pasting temperature, and setback during cooling that can be considered as valuable predictors, at a dough level, of bread firming behaviour during storage. Individual and/or binary addition of surfactants to bread dough, particularly MGL and SSL, positively influence the level of the pasting parameters associated with a significant delay in bread firming. Individual additions of methylcellulose derivatives, mainly CMC, induce in general a deleterious effect on dough viscosity. Moreover, the simultaneous presence of CMC and HPMC results in a significant improvement of dough rheology during cooling. Binary mixtures SSL/CMC and MGL/CMC are not recommended from the viscoelastic point of view, due to antagonistic effects of the pair gum/surfactant that nullify the benefits of individual emulsifiers.

Key words Pasting properties \cdot Non-fat additives \cdot Fat additives · Bread quality prediction · Bread staling

Introduction

Changes in the viscosity of highly hydrated starch-based systems such as doughs during baking are known to affect

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the viscoelastic behaviour and the texture and keepability of finished bread [1]. Pasting performance of wheat flours during cooking and cooling involves many processes such as swelling, deformation, fragmentation, and solubilisation that occur in a very complex media whose viscoelastic properties in the pasted and gelled states are governed primarily by the volume occupied by the swollen particles [2]. The multiplicity of reactions and interreactions during the baking process as well as the presence of biochemical constituents other than the starch, the added ingredients, additives and technological aids favour viscosity changes of dough systems, and thus affect baking performance and staling behaviour of bread.

The pasting properties of cereal flours are known to be affected by pentosans, fatty acids, surfactants and fats [3], residual protein of the starch granules and gluten [1], through competition of hydratable components with starch for water, and/or complexation with starch [4]. Sugars [5], salt, skim milk, shortening, oxidising and reducing agents, mould inhibitors [6, 7] and non-starch polysaccharides [8] also modify the gelatinisation behaviour of wheat starch and/or retrogradation of bread crumbs.

Changes in rheological behaviour occur during starch gelatinisation with lipids addition to starch [9, 10, 11, 12]. The formation of an inclusion complex between amylose and fatty acids [13] or the hydrocarbon chain of the added emulsifiers [14] and native lipids [15] has been confirmed, and recent evidence supports the theory that the outer branches of amylopectin can complex lipids [16]. It has been demonstrated that an increase in amylose-lipid complexation results in a decrease in the amylopectin retrogradation [17] and in an increase of the Avrami exponent, indicating slower crumb firming kinetics at short storage periods [18].

Formation of amylose-lipid complexes alters the gelatinisation and pasting characteristics of starches [12]. In general, granule swelling was delayed and solubilisation of amylose was reduced in the presence of a ligand-containing molecule [19, 20]. Gelatinisation temperature of the starch may or not be changed [21], and upon cooling, starch gels made with surfactants were

found to be weaker. Amylose-lipid complex formation caused a reduction in starch swelling and of starch solubles leached, thus affecting the rheological behaviour of starch pastes [14, 19]. Usually, gels with high amounts of emulsifier are weak [22], functioning to soften the cake/bread crumb. This may be because less amylose leaches from the granules to bind with itself, and so is not available to form the rigid gel structure via hydrogen bonding upon cooling. The degree to which emulsifiers complex with amylose depends on the length of the fatty acid chain, the degree of unsaturation and the composition of the hydrophilic region [23] as well as the phase composition of the emulsifier and lipid monomer concentration [24]. The extent of the amylose-lipid complexation can be measured as the energy required for dissociating the amylose-lipid complex and as the increase in viscosity during the cooling of starch paste [25]. Both thermal and rheological measurements of the amylose complexation can be used at dough level as indirect methods to predict bread staling [26].

Hydrocolloids that improve fresh bread quality and delay bread staleness [27] can significantly affect both the cooking and cooling rheology of starch systems [28]. Viscosity of starch/hydrocolloid systems after heating and cooling is greater than in starch-only systems [29] due in part to changes in granule size or shape during swelling and to the release of amylose and LMW amylopectin which promotes the formation of polymer complexes and significantly adds to the viscosity of the system [30]. Starch gelation takes place upon cooling and is strongly influenced by the gelation of amylose, which is modified by the added hydrocolloid. It has also been proposed that diffusion of media water from the continuous phase into the starch granules increases the gum concentration surrounding them [31]. Possibly, both mechanisms are involved. In addition, the presence of hydrocolloids changed the α -amylase/starch interactions, modifying the hydrolytic activity of the enzyme on the starch [32].

The Brabender visco-amylograph (BVA) has traditionally been used to measure the pasting profile of starches for screening and quality control, and to provide product specifications [33] particularly to discriminate between slightly different pasting profiles [34]. Amylogram parameters related to lipid-starch complex evaluation correlate highly with firming kinetic parameters [27] and lipid binding in doughs [35] and stored breads [36]. More recently, alternative instruments have been developed to overcome some disadvantages, such as long analysis time and the need for a large sample size [37, 38], and the use of arbitrary viscosity units [39]. The Rapid Visco Analyser (RVA) [40] drastically reduces both the sample quantity and the analysis time needed. Some comparative studies have been performed between the BVA and the RVA with only significant correlations for peak and end viscosities [38, 41] for native unmodified starch samples, and good correlations for viscosity data for most modified starches [34] No good correlation of the temperature data has been reported and results were less similar for flours.

The purpose of this paper was to investigate: (1) the viability of the RVA in studying the effects of additives on the viscosimetric properties of formulated wheat doughs, (2) the single and/or interactive effects of surfactants and hydrocolloids on the pasting profile of doughs, and (3) the significance of the viscosity profile of formulated doughs as a predictor of staling behaviour of breads.

Materials and methods

Basic ingredients and additives. A commercial blend of Spanish wheat flours (13.98% moisture, 1.72% ash content, 12.96% protein, 78% gluten index, pasting temperature 77 °C, peak viscosity 120 Brabender units $(B\bar{U})$, setback 95° C) was used.

Freeze dried cultures of *Lactobacillus brevis*, 25A (BGKF, Detmold, Germany) (10¹¹ colony forming units (cfu)/g), *L*. plantarum, B-39 (Cereals laboratory Collection) (10^{10} cfu/g) , multiform commercial Detmold-83 (CHR Hansen's Laboratorium A/S, Denmark) consisting of L. brevis:L. plantarum:L. fructivorans $(1:1:1, 10⁹$ cfu/g), and commercial compressed yeast (CCY) $(10¹⁰$ cells/g, dry matter) were used as starters. Bacterial starters were propagated and furnished "ready-to-use" by CHR Hansen's Laboratorium.

Emulsifiers (Grinsted, Denmark) included AMIDAN SDM-T distilled vegetable monoglycerides in powder form (MGL), PAN-ODAN 80 diacetyl tartaric acid ester of mono-diglycerides in fine powder (DATEM), and ARTODAN SP 55 sodium stearoyl lactylate in small beds (SSL). Hydrocolloids (Aqualon, France; Dow Chemical, USA) were respectively Blanose cellulose gum purified sodium carboxymethylcellulose (CMC) and Methocel K 4 M hydroxypropylmethylcellulose (HPMC). Fungamyl 180S (Novo Nordisk Bioindustrial, Spain) fungal α -amylase was used.

Doughs and breads preparation. Basic dough formula on 100 g flour basis consisted of salt (1.8 g), CCY (2 g), bacterial starter (10^8 bacteria), calcium propionate (0.20 g) and water (up to 500 BU consistency). Process variables (qualitative and quantitative independent factors) tested at two levels (0, 1) included breadmaking process (straight, sour dough), bacterial starter (B39+25A, Detmold-83), MGL (0, 0.3%), DATEM (0, 0.3%), SSL (0, 0.5%), CMC (0, 0.3%), HPMC (0, 0.3%) and α -amylase (0, 125 SKB). Sour doughs (sour dough process) were prepared by hand mixing of ingredients flour (100 g), water (100 ml), bacterial inoculum ($10⁹$ bacteria), and yeast inoculum (10⁸ cells)—and fermentation for 20 h at 30 $^{\circ}$ C before inoculation at 10% into bread doughs [42]. Formulated unfermented bread doughs (UF) were prepared by mixing ingredients (basic and additives) in a 10 kg arm mixer at 60 turns/min up to optimum dough development. Fermented doughs (F) were obtained after two-step bulk-fermentation and proofing up to maximum volume increment and baked at 190 $^{\circ}$ C for 20 min to make breads. After cooling for 1 h, breads were packaged in co-extruded polypropylene bags and stored for 1, 3, 7, 10 and 15 days at 24 ± 1 °C.

Rheological properties. Rheological profiles of doughs were determined by farinograph, extensigraph [43], maturograph and oven rise recorder (Brabender guidelines) in rheological Brabender equipment (Duistburg, Germany) [44].

Pasting properties. The pasting profiles—gelatinisation, pasting and setback properties—were obtained with both a standard Brabender visco-amylograph (BVA) [25] and a Newport rapid viscoanalyser (RVA) [45] using freeze-dried formulated dough samples (BVA: 45 g, dry basis and 450 ml distilled water; RVA: 3.5 g, 14% moisture basis and 25 ml distilled water). Pasting parameters were determined in both viscographs (BVA, RVA) for pasting temperature (centigrade, centigrade), peak viscosity (Brabender units, centipoise), peak temperature (centigrade, centigrade), viscosity at 95° C (Brabender units, centipoise), holding (Brabender units, centipoise), breakdown (Brabender units, centipoise), viscosity at 50 $\mathrm{^{\circ}C}$ (Brabender units, centipoise), and setback on cooling (Brabender units, centipoise) using standard test profiles (1 h 54 min, 13 min).

Physico-chemical properties. The gluten index of UF was determined following ICC methodology [46]. Bread texture as the maximum deformation strength (highest peak in deformation curve, in grams.) was recorded in an Instron press, model 1140 (Instron Food Testing Machine, USA) using a 2.5 cm diameter universal cell, 0.5–5 kg header, and 75% penetration depth, on 2 cm width slices from the center of the loaf [47].

Sensory analysis. Sensory analysis of fresh breads was performed with a panel of five trained judges using semi structured scales, scored 1–10, in which extremes were described. Evaluated attributes were: crumb structure, (extremes: uneven and compacted alveoles-even and opened alveoles), grain, (rough-smooth), elasticity, (hard and inelastic-soft and elastic), crumb eatability, (gummy, rough and inelastic-edible, smooth and elastic), crust eatability, (chewy and gummy-crunchy), smell intensity, (slight, bland-strong), typical smell, (odd-typical and characteristic), taste intensity, (slight, bland-strong), typical taste (odd-typical and characteristic) and overall acceptability (unpleasant-pleasant).

Avrami parameters. Values for the Avrami model factors $\theta = \frac{T_{\infty} - T_t}{T_{\infty} - T_0} = e^{-kt^n}$ where θ is the fraction of the recrystallisation still to occur; T_0 , T_∞ and T_t are crumb firmness at zero time, ∞ and "t" time; k is a rate constant (usually used $1/k$ = time constant to compare bread firming rate), and n is the Avrami exponent) were estimated by fitting experimental points into non-linear regression equations [18].

Statistical analysis. Samples for dough preparation to analyse breadmaking process and additive single effects and interactions

Fig. 1 Plots of pasting behaviour of formulated doughs recorded at the Newport rapid visco analyser. See Table 1 for sample composition. cP Centipoise

Table 1 Saturated factorial design L_{16} for sampling. Levels $(0, 1)$ of factors (A to H): A=process: straight (0), sourdough (1); B=MGL: none (0), 0.3% flour basis (1); C=DATEM: none (0), 0.3% flour basis (1); D=SSL: none (0) , 0.5% flour basis (1) ; E= CMC: none (0) , 0.3% flour basis (1); $F = \alpha$ -amylase: none (0), 125 SKB (1); $G =$ starter: B-39+25A (0), Detmold–83 (1); H= HPMC: none (0), 0.3% flour basis (1).

Sample No.	Level of design factors ^a							
	A	B	\mathcal{C}	D	E	F	G	H
2								
3								
$\frac{4}{5}$								
6								
8								
9								
10								
11								
12								
13								
14								
15								
16								

were made following a fractionated factorial design structure Taguchi L16 [48] disclosed in Table 1. Multivariate (correlation matrix, multiple analysis of variance, multiple regressions) and univariate analysis (single regressions) were both performed by using Statgraphics V.7 program (Bitstream, Cambridge, Mass, 1992).

Results and discussion

Significance of the viscosity profile of formulated doughs as a predictor of staling behaviour of breads

Qualitative pasting profile during cooking and cooling of formulated wheat doughs according to a fractionated factorial design (Table 1) closely depends on dough composition (Fig. 1), particularly on the presence/absence of surfactants and hydrocolloids of different molecular structures. These design factors also define some fresh bread quality characteristics [27, 47, 48] and condition bread keeping behaviour during storage [18, 27]. The effects particularly affect the initial crumb firmness and the sensory scores of fresh bread and the degree and rate of firming/staling. Bread staling during storage follows the Avrami equation in which the n (Avrami exponent)

and k (rate constant) parameters govern staling kinetics. Suitable trends for slow staling rate correspond to low k and high *n* values as described before [18, 35, 36]. In this research, the correspondence between staling kinetics (finished bread) and the pasting behaviour (dough level) was statistically significant $(\alpha < 0.05)$ showing close relationships between viscoelastic and kinetic parameters (Fig. 2). Suitable viscosimetric trends at dough level to delay bread staling include delayed pasting temperature, high viscosities that characterise changes during pasting and gelling and low paste viscosity at 95° C. These viscosity trends are also in good agreement for high sensory scores of fresh bread obtained for both crumb and crust eatability that highly $(\alpha < 0.05)$ and positively correlated (correlation coefficient r) with holding $(r=$ 0.6042), viscosity at end of holding at 50 °C ($r=0.5823$),

Fig. 2 Relationships between pasting parameters of formulated doughs and staling kineticsof breads thereof. r Correlation coefficient, α significance level Fig. 3 Relationships between pasting properties of formulated doughs from Newport rapid visco analyser (RVA) and Brabender visco amilograph (BVA).r Correlation coefficient, α significance level

Table 2 Correlation coefficients among pasting parameters of formulated doughs set at the Newport rapid viscoanalyser

* $P \le 0.05$; ** $P \le 0.01$

and partial $(r=0.5944)$ and total setback $(r=0.5944)$ on cooling.

Effects of design factors on the pasting parameters of formulated wheat doughs.

Relationships between pasting parameters recorded at the RVA and the BVA respectively were particularly highly significant $(\alpha<0.01)$ for parameters characterising starch cooling behaviour: viscosity at 50 \degree C, viscosity at end of holding at 50 \degree C, and partial and total setback on cooling (Fig. 3). Poor correlations were found for viscosity and temperature data characterising starch gelatinisation and pasting processes during cooking as stated before [34], mainly attributed to the different time-temperature profiles used [49] for RVA and BVA and the use of arbitrary viscosity units in BVA. This last is probably the main reason responsible for the lack of statistically meaningful differences of design factors—mainly breadmaking process, CMC and bacterial starter—on some pasting properties when BVA is used compared with RVA (Table 3). Conversely, pasting parameters during cooking and cooling of formulated doughs set at RVA significantly and positively correlated except for pasting temperature versus peak viscosity, viscosity at 95 \degree C and breakdown that observed negative relationships (Table 2). In general, correlation coefficients (r) were higher among parameters

*P<0.05; **P<0.01

 $*P<0.05$; $*P<0.01$

Table 3 Single effects of design factors on pasting parameters of formulated doughs set at the Newport rapid viscoanalyser (RVA) and at the Brabender visco-amylograph (BVA). BU Table 3 Single effects of design factors on pasting parameters of formulated doughs set at the Newport rapid viscoanalyser (RVA) and at the Brabender visco-amylograph (BVA). BU

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characterising cooling starch behaviour $(r>0.8)$ than those for starch cooking $(r<0.8)$. Parameters derived from pasted and gelled doughs strongly correlated as well, particularly peak viscosity, viscosity at end of holding, holding and setback.

The quantitative single and interactive effects of design factors—breadmaking process, surfactants, hydrocolloids, α -amylase and bacterial starter—on pasting parameters are given in Table 3 and Table 4 respectively.

Effects on the cooking starch properties (pasting/gelatinisation)

Major effects on cooking parameters were provided by surfactants and hydrocolloids (Table 3). Individual addition of surfactants to the dough, particularly MGL and SSL induced, in general, suitable trends in the viscosity parameters concerning pasting and paste cooking. Effects were more pronounced for increasing peak viscosity, viscosity at end of holding at 95 \degree C (MGL) and pasting temperature (SSL). The extent of hydrocolloid effects was not as prominent as surfactant action which induced particularly significant and unsuitable effects in decreasing peak viscosity and viscosity at the end of holding at 95 \degree C (CMC) that resulted in decreased holding and breakdown on cooking. The simultaneous presence of two surfactants provided different effects: in MGL-containing doughs, SSL addition promoted maximum viscosity increase whereas DATEM inclusion gave doughs with higher viscosity at the end of holding at 95 \degree C (Table 4). Binary mixtures surfactant/hydrocolloid particularly MGL/CMC and SSL/CMC led to unsuitable interactive effects, mainly on maximum viscosity and pasting temperature.

Effects on the cooling starch properties (gelling)

Cold paste viscosity and setback on cooling, characteristics strongly associated with bread staling kinetics (Fig. 2), closely depended on the single and/or binary addition to dough formulation of hydrocolloids and surfactants. The effects of the breadmaking process, α amylase and bacterial starter on cooling starch profile, were not relevant (Table 3, Table 4) Single and/or associated mixtures of MGL and SSL resulted in beneficial viscosity trends, mainly on setback increase. Single addition of hydrocolloids was in general not advisable, whereas CMC/HPMC association resulted in partial amelioration of unsuitable single effects on setback. CMC addition to SSL-containing doughs was disregarded due to antagonistic effects of the pair gum-surfactant.

The conclusions which can be drawn from this work are:

-1. Bread dough viscosity characteristics derived from the RVA pasting profile during cooking and cooling highly correlate with bread staling kinetic parameters.

This particularly so in the cases of peak viscosity, pasting temperature, and setback during cooling that can be considered as valuable predictors at dough level of bread firming behaviour during storage.

- -2. Individual and/or binary addition of surfactants to bread dough, particularly MGL and SSL positively influence the level of the pasting parameters associated with a significant delay in bread firming.
- -3. Individual addition of methylcellulose derivatives, mainly CMC, induce in general a deleterious effect on dough viscosity. Moreover, the simultaneous presence of CMC and HPMC results in a significant improvement of dough rheology during cooling.
- -4. Binary mixtures SSL/CMC and MGL/CMC are not recommended from the viscoelastic point of view due to antagonistic effects of the pair gum/surfactant that nullify the benefits of individual emulsifiers.

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